



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/07876 <b>(22) International Filing Date:</b> 09 April 1999 (09.04.1999) <b>(30) Priority Data:</b> 60/118,799 04 February 1999 (04.02.1999) US <b>(60) Parent Application or Grant</b> THE DOW CHEMICAL COMPANY [/]; O. INBASEKARAN, Michael [/]; O. WOO, Edmund, P. [/]; O. WU, Weishi [/]; O. BERNIUS, Mark, T. [/]; O. ZERULL, Susan, Moeller; O.		<b>Published</b>  <b>BEST AVAILABLE COPY</b>
<b>(54) Title: FLUORENE COPOLYMERS AND DEVICES MADE THEREFROM</b> <b>(54) Titre: COPOLYMERES DE FLUORENE ET DISPOSITIFS FABRIQUES A PARTIR DE CEUX-CI</b>  <b>(57) Abstract</b> This invention relates to: (a) fluorene copolymers comprising at least 10 percent (by residual monomeric units) of 9-substituted and/or 9,9-disubstituted fluorene moieties and at least two other monomeric units containing delocalized p-electrons, (b) polymer blends comprising at least 10 weight percent of a copolymer specified in (a), and (c) electronic devices (such as polymer light emitting diodes) containing one or more films derived from these copolymers.  <b>(57) Abrégé</b> L'invention concerne: (a) des copolymères de fluorène comprenant au moins 10 pour cent (par motif monomère résiduel) de parties fluorène substituées en position 9 et bisubstituées en position 9, 9, et au moins deux autres motifs monomères contenant des électrons p délocalisés; (b) des mélanges polymères comprenant au moins 10 pour cent en poids d'un copolymère spécifié dans (a); et (c) des dispositifs électroniques (tels que des diodes électroluminescentes polymères) contenant un ou plusieurs films dérivés de ces copolymères.		

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<b>(54) Title:</b> FLUORENE COPOLYMERS AND DEVICES MADE THEREFROM  <b>(57) Abstract</b>  This invention relates to: (a) fluorene copolymers comprising at least 10 percent (by residual monomeric units) of 9-substituted and/or 9,9-disubstituted fluorene moieties and at least two other monomeric units containing delocalized p-electrons, (b) polymer blends comprising at least 10 weight percent of a copolymer specified in (a), and (c) electronic devices (such as polymer light emitting diodes) containing one or more films derived from these copolymers.		

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## Description

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## FLUORENE COPOLYMERS AND DEVICES MADE THEREFROM

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This application is under Government contract with the Naval Air Warfare Center #N00421-98C-1187.

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This invention relates to fluorene copolymers, polymer blends comprising such copolymers, and electronic devices (such as polymer light emitting diodes) containing one or more films derived from these copolymers.

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Conjugated polymers may exhibit the optical and electronic properties of inorganic semiconductors because of the presence of delocalized p-electrons. Poly(9,9-disubstituted-fluorene-2,7-diyls) constitute a family of semiconducting polymers with advantageous features. Their aromatic backbone is resistant to chemical and photochemical degradation; the biphenylene unit of each fluorene monomer is locked into a planar-like configuration by the C9 atom; substituents on C9 may be chosen to modify physical and chemical properties without introducing torsional strain between adjacent fluorene units which would otherwise be disruptive to delocalization of the p-system. Indeed, poly(9,9-di-n-octylfluorene-2,7-diyl) of U.S. Patent 5,708,130 has been shown to be an effective emitter for a blue light emitting diode (LED) (Grice, et.al, Applied Physics Letters, Vol. 73, 1998, p. 629-631) and to exhibit high carrier mobility, a very desirable feature for electronic devices (Redecker, et. al., Applied Physics Letters, Vol. 73, 1998, p. 1565-1567.

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A means to further modify their optical and electronic properties is desired in order to broaden the applicability of these fluorene polymers in electronic devices. In this context, optical properties of a polymer include its absorption and photoluminescence spectra and electronic properties include ionization potential, electron affinity, band gap and carrier transport and mobility. U.S. Patent Application Serial Number 08/861,469, filed May 21, 1997, teaches a way for property modification via fluorene copolymers each containing 9,9-disubstituted fluorene and another comonomer. For instance, copolymers comprising fluorene and aromatic amines have lower (closer to vacuum level) ionization potential and preferential hole transporting properties, and copolymers with cyano-containing moieties have higher electron affinity and preferential electron transporting properties relative to fluorene homopolymers.

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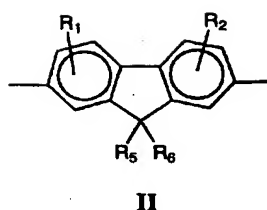
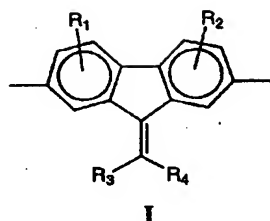
Many electronic applications require the active material to exhibit both hole transporting and electron transporting properties. To maximize the efficiency of a LED, for example, the polymer should ideally transport both holes and electrons equally well

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5 (Bradley et. al., in Springer Series in Solid State Sciences, Vol 107, Springer-Verlag  
Berlin Heidelberg, 1992, p. 304-309). The copolymers of United States Patent  
10 Application Serial Number 08/861,469 filed May 21, 1997, comprising a fluorene moiety  
and one other comonomer cannot meet this requirement; therefore, there is a need for  
5 further improvement.

15 This invention relates to copolymers of 9-substituted and/or 9,9-disubstituted  
fluorene moieties and at least two other comonomers containing delocalized p-electrons.  
Preferably, at least 10 percent of the total monomeric units of these copolymers are  
selected from 9-substituted- and/or 9,9-disubstituted fluorenes; more preferably at least  
10 15 percent of the monomeric units of these copolymers are selected from 9-substituted-  
and/or 9,9-disubstituted fluorenes; and most preferably at least 20 percent of the  
20 monomeric units of these copolymers are selected from 9-substituted- and/or 9,9-  
disubstituted fluorenes. Each copolymer contains two or more non-fluorene comonomers  
in any proportion. These copolymers are characterized by their excellent solubility (>1  
25 g/L) in common organic solvents, ability to form pin-hole free films and weight-average  
molecular weight of at least 3000 gram/mole relative to polystyrene standard, preferably  
at least 10,000 gram/mole, most preferably at least 20,000 gram/mole. They are further  
30 characterized by a polydispersity of less than 10, preferably less than 5, most preferably  
less than 3. These copolymers exhibit photoluminescent emission in the range of 350  
20 nm to 1,000 nm and absorption from 200 nm to 600 nm. The copolymers of this  
invention are useful as the active components in electronic devices including light  
35 emitting diodes, photocells, photoconductors, and field effect transistors.

40 This invention relates to fluorene copolymers and electronic devices comprising a  
film of such copolymers. The subject copolymers comprise at least 10 percent, based on  
25 residual monomeric units (RMU), of 9-substituted and/or 9,9-disubstituted fluorene  
moieties represented by structures I and II respectively. A residual monomeric unit is the  
portion of the monomer that is incorporated into the polymer backbone. For instance,  
1,4-phenylene is the residual monomeric unit of 1,4-difunctional-benzene monomers  
45 irrespective of the chemical nature of the functional groups.



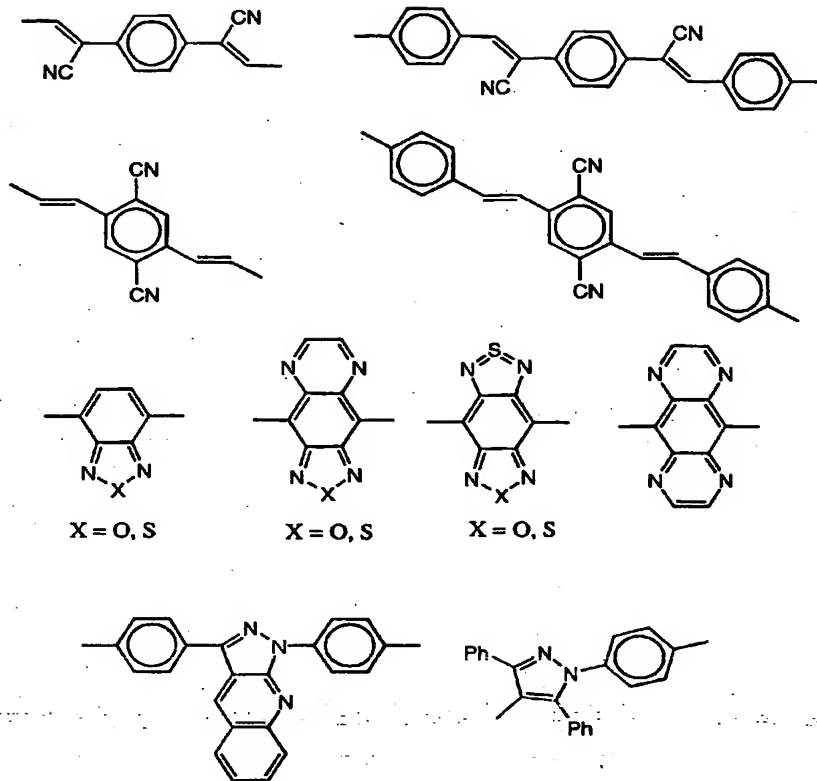
In structures I and II,  $R_1$  and  $R_2$  are independently in each occurrence hydrogen,  $C_{1-20}$  hydrocarbyl,  $C_{1-20}$  hydrocarbyloxy,  $C_{1-20}$  thiohydrocarbyloxy, or cyano.  $R_1$  and  $R_2$  are independently in each occurrence preferably hydrogen,  $C_{1-20}$  alkyl,  $C_{6-10}$  aryl or alkyl-substituted aryl,  $C_{6-10}$  aryloxy or alkyl-substituted aryloxy,  $C_{1-12}$  alkoxy/thioalkoxy, and cyano. Even more preferably  $R_1$  and  $R_2$  are independently in each occurrence hydrogen,  $C_{1-10}$  alkyl, phenyl, and cyano.  $R_3$  and  $R_4$  are independently in each occurrence a hydrogen,  $C_{1-20}$  hydrocarbyl optionally substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters;  $C_{6-20}$  aryl optionally substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters.  $R_3$  and  $R_4$  may also form  $C_{3-12}$  cyclic structures with the olefin carbon (structure I) to which they are attached, said cyclic structures may further contain one or more heteroatoms such as phosphorus, sulfur, oxygen and nitrogen. Preferably  $R_3$  and  $R_4$  are independently in each occurrence a hydrogen,  $C_{1-12}$  alkyl optionally substituted with  $C_{1-12}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano and esters;  $C_{6-20}$  aryl optionally substituted with  $C_{1-12}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters. Most preferably  $R_3$  and  $R_4$  are independently in each occurrence a hydrogen,  $C_{1-8}$  alkyl optionally substituted with  $C_{1-10}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters;  $C_{6-12}$  aryl optionally substituted with  $C_{1-10}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters.  $R_5$  and  $R_6$  are independently in each occurrence a hydrogen,  $C_{1-20}$  hydrocarbyl optionally substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters;  $C_{6-20}$  aryl optionally substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters.  $R_5$  and  $R_6$  may also form  $C_{3-12}$  cyclic structures with the C-9 carbon of

fluorene (structure II), said cyclic structures may further contain one or more heteroatoms such as phosphorus, sulfur, oxygen and nitrogen. Preferably  $R_1$  and  $R_2$  are independently in each occurrence a hydrogen,  $C_{1-12}$  alkyl optionally substituted with  $C_{1-12}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano and esters;  $C_{6-20}$  aryl optionally substituted with  $C_{1-12}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters. Most preferably  $R_1$  and  $R_2$  are independently in each occurrence a hydrogen,  $C_{1-6}$  alkyl optionally substituted with  $C_{1-10}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters;  $C_{6-12}$  aryl optionally substituted with  $C_{1-10}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters. These copolymers are characterized by their excellent solubility ( $>1$  g/L) in common organic solvents, ability to form pin-hole free films and weight-average molecular weight of at least 3,000 gram/mole relative to polystyrene standard, preferably at least 10,000 gram/mole, most preferably at least 20,000 gram/mole. They are further characterized by a polydispersity of less than 10, preferably less than 5, most preferably less than 3. These copolymers exhibit photoluminescent emission in the range of 350 nm to 1,000 nm and absorption from 200 nm to 600 nm. The copolymers of this invention are useful as the active components in electronic devices including light emitting diodes, photocells, photoconductors, and field effect transistors.

In the first embodiment, the copolymers of the invention comprise at least 10 percent RMU of structures I and/or II and at least 1 percent of two or more RMUs possessing hole transporting property. Hole transporting property is imparted to a polymer by electron-rich RMUs. Examples include those derived from stilbenes or 1,4-dienes without electron-withdrawing substituents, tertiary amines,  $N,N,N',N'$ -tetraaryl-1,4-diaminobenzene,  $N,N,N',N'$ -tetraarylbenzidine,  $N$ -substituted-carbazoles, diarylsilanes, and thiophenes/furans/pyrroles without electron-withdrawing substituents. These hole transporting RMUs may bear a variety of substituents so long as their presence do not significantly affect hole transporting properties adversely. Preferred substituents are  $C_{1-20}$  alkyls,  $C_{6-20}$  aryls and alkylaryls optionally substituted with  $C_{1-6}$  alkoxys and  $C_{6-12}$  aryloxys. Particularly effective are RMUs derived from tertiary aromatic amines,  $N,N,N',N'$ -tetraaryl-1,4-diaminobenzene,  $N,N,N',N'$ -tetraarylbenzidine, thiophene, and bithiophene. Preferably the copolymers comprise at least 15 percent of RMUs of structures I and/or II,

5 and at least 10 percent of two or more hole transporting RMUs. Most preferably the copolymers comprise at least 20 percent of RMUs of structures I and/or II and at least 20 percent of two or more RMUs possessing hole transporting property. The ratio of I to II  
10 may vary without limit and similarly the ratio of various hole transporting RMUs can vary without limit so long as the combined percentage in the copolymer remains within the specified range. With respect to the hole transporting RMUs in the copolymers of the invention, there is no restriction that they must all belong to the same chemical type. A  
15 copolymer of the invention may, for example, contain RMUs of the silanyl type, RMUs of the thiophene type and RMUs of the tertiary amine type.

10 In the second embodiment the copolymers of the invention comprise at least 10 percent of RMUs of structures I and II and at least 1 percent of two or more RMUs possessing electron transporting property. Electron transporting property is imparted to  
20 polymers by electron-deficient RMUs. Examples include RMUs containing electron-withdrawing groups such as F, cyano, sulfonyl, carbonyl, nitro, carboxy; moieties containing imine linkage, and condensed polycyclic aromatics. Condensed polycyclic  
25 aromatics include acenaphthene, phenanthrene, anthracene, fluoranthene, pyrene, perylene, rubrene, chrysene, and corene. Five-membered heterocycles containing imine linkages include oxazoles/isoxazoles, N-substituted-imidazoles/pyrazoles, thiazole/isothiazole, oxadiazoles, and N-substituted-triazoles. Six-membered  
30 heterocycles containing imine linkages include pyridines, pyridazines, pyrimidines, pyrazines, triazines, and tetrazenes. Benzo-fused heterocycles containing imine linkages include benzoxazoles, benzothiazole, benzimidazoles, quinoline, isoquinolines, cinnolines, quinazolines, quinoxalines, phthalazines, benzothiadiazoles, benzotriazines, phenazines, phenanthridines, and, acridines. More complex RMUs include 1,4-  
35 tetrafluorophenylene, 1,4'-octafluorobiphenylene, 1,4-cyanophenylene, 1,4-dicyanophenylene, and  
40



These electron transporting RMUs may bear a variety of substituents so long as their presence does not significantly affect electron transporting properties adversely. Preferred substituents are  $C_{1-20}$  alkyls,  $C_{6-20}$  aryls and alkylaryl optionally substituted with  $C_{1-8}$  alkoxy and  $C_{6-12}$  aryloxy. Particularly effective are RMUs derived from perfluorobiphenyl, quinoxalines, cyano-substituted olefins, oxadiazole, and benzothiadiazoles. Preferably the copolymers comprise at least 15 percent of RMUs of structures I and/or II, and at least 10 percent of two or more of the exemplified electron transporting RMUs. Most preferably the copolymers comprise at least 20 percent of RMUs of structures I and/or II and at least 20 percent of two or more of the exemplified electron transporting RMUs. The ratio of I to II can vary without limit and similarly the ratio of various electron transporting RMUs may vary without limit so long as the combined percentage in the copolymer remains within the specified range. With respect

5 to the electron transporting RMUs in the copolymers of the invention, there is no  
restriction that they must all belong to the same chemical type. A copolymer of the  
invention may, for example, contain RMUs of the cyano-olefin type, RMUs of the  
10 oxadiazole type and RMUs of the condensed polynuclear aromatic type.

5 In the third embodiment, copolymers of the invention comprise at least 10 percent  
of RMUs of structures I and/or II and at least 1 percent of one or more hole transporting  
15 RMUs and at least 1 percent of one or more electron-transporting RMUs. Hole  
transporting RMUs and electron transporting RMUs are selected from among those  
already defined above. More preferably copolymers of this embodiment comprise at  
10 least 15 percent of RMUs of structures I and/or II and at least 5 percent of one or more  
hole transporting RMUs and at least 5 percent of one or more electron-transporting  
20 RMUs. Most preferably copolymers of this embodiment comprise at least 20 percent of  
RMUs of structures I and/or II and at least 10 percent of one or more hole transporting  
RMUs and at least 10 percent of one or more electron-transporting RMUs. The ratio of I  
25 to II can vary without limit and similarly the ratio of various hole transporting RMUs may  
vary without limit so long as the combined percentage in the copolymer remains within  
the specified range. With respect to the hole transporting RMUs in the copolymers of the  
invention, there is no restriction that they must all belong to the same chemical type. A  
30 copolymer of the invention may, for example, contain RMUs of the silanyl type, RMUs of  
the thiophene type and RMUs of the tertiary amine type. Similarly, with respect to the  
electron transporting RMUs in the copolymers of the invention, there is no restriction that  
they must all belong to the same chemical type. A copolymer of the invention may, for  
35 example, contain RMUs of the cyano-olefin type, RMUs of the oxadiazole type and RMUs  
of the condensed polynuclear aromatic type.

25 In the fourth embodiment, copolymers of the invention comprise at least 10  
percent of RMUs of structures I and/or II, at least 1 percent of one or more RMUs  
40 derived independently in each occurrence from benzene, naphthalene, and biphenylene  
optionally substituted with  $C_{1-12}$  alkyl/alkoxy and  $C_{6-10}$  aryl/aryloxy (hereinafter referred to  
as arylene RMUs), and at least 1 percent of one or more RMUs selected from among the  
45 hole transporting and electron transporting RMUs defined above. Preferably copolymers  
30 of this embodiment comprise at least 15 percent of RMUs of structures I and/or II; at  
least 5 percent of one or more arylene RMUs, and at least 1 percent of one or more  
RMUs selected from among the hole transporting and electron transporting RMUs  
50 defined above. Most preferably copolymers of this embodiment comprise at least 20

5 percent of RMUs of structures I and/or II, at least 10 percent of one or more arylene  
RMUs, and at least 5 percent of one or more RMUs selected from among the hole  
10 transporting and electron transporting RMUs defined above. The ratio of I to II can vary  
without limit and similarly the ratio of various arylene RMUs may vary without limit so long  
5 as the combined percentage in the copolymer remains within the specified range.  
Incorporation of arylene RMUs can lead to modifications in the thermal, optical and  
15 electronic properties of the copolymers.

20 The fifth embodiment relates to blends of two or more of the copolymers of the  
invention without limits on relative proportions of the individual components. Such blends  
may be prepared by solution blending, or blending in the melt state.

25 The sixth embodiment relates to blends containing at least 0.1 weight percent of  
at least one copolymer of the invention with at least one of the fluorene homopolymers or  
copolymers disclosed in US 5,708,130, US 5,777,070, and U.S. Application Serial No.  
08/861,469. Such blends may be prepared by solution blending, or blending in the melt  
15 state.

30 The seventh embodiment relates to blends containing at least 0.1 weight percent  
of at least one copolymer of the invention with at least one other non-fluorene polymer,  
for example, polystyrene, polyethylené, poly(methyl methacrylate), polysulfones,  
polycarbonates, and polyurethanes. Such blends may be prepared by solution blending,  
20 or blending in the melt state.

35 The eighth embodiment relates to a film containing at least 0.1 weight percent of  
at least one copolymer of the invention.

40 The ninth embodiment of the invention relates to light emitting diodes comprising  
one or more of the copolymers of the invention wherein the copolymers are present as  
25 single-layer films or as multiple-layer films, whose combined thickness is in the range of  
10 nm to 1000 nm, preferably in the range of 25 nm to 500 nm, most preferably in the  
range of 50 nm to 300 nm. The copolymer films may be formed by solvent-based  
45 processing techniques such as spin-coating, roller-coating, dip-coating, spray-coating,  
and doctor-blading. When two or more copolymers are used, they may be deposited  
30 separately as distinct layers or deposited as one layer from a solution containing a blend  
of the desired copolymers. An organic light emitting diode typically consists of an organic  
50 film sandwiched between an anode and a cathode, such that when a positive bias is  
applied to the device, holes are injected into the organic film from the anode and

5 electrons are injected into the organic film from the cathode. The combination of a hole  
and an electron may give rise to an exciton which may undergo radiative decay to the  
10 ground state by releasing a photon. The anode and the cathode may be made of any  
materials and in any structure known in the art. The anode is preferably transparent. A  
5 mixed oxide of tin and indium (ITO) is useful as the anode due to its conductivity and  
transparency. ITO is deposited on a transparent substrate such as glass or plastic so  
15 that the light emitted by the organic film may be observed. The organic film may be the  
composite of several individual layers or may be the blend of several materials each  
designed for a specific function. The cathode is commonly a metallic film deposited on  
10 the surface of the organic film by either evaporation or sputtering.

20 The tenth embodiment of the invention relates to photocells comprising one or  
more of the copolymers of the invention wherein the copolymers are present as single-  
layer films or as multiple-layer films, whose combined thickness is in the range of 10 nm  
to 1000 nm, preferably in the range of 25 nm to 500 nm, most preferably in the range of  
25 50 nm to 300 nm. The copolymer films may be formed by solvent-based processing  
techniques such as spin-coating, roller-coating, dip-coating, spray-coating and doctor-  
blading. When two or more copolymers are used, they may be deposited separately as  
distinct layers or deposited as one layer from a solution containing a blend of the desired  
30 copolymers. By photocells is meant a class of optoelectronic devices which can convert  
incident light energy into electrical energy. Examples of photocells are photovoltaic  
devices, solar cells, photodiodes, and photodetectors. A photocell generally comprises a  
transparent or semi-transparent first electrode deposited on a transparent substrate. A  
35 polymer film is then formed onto the first electrode which is, in turn, coated by a second  
electrode. Incident light transmitted through the substrate and the first electrode is  
25 converted by the polymer film into excitons which can dissociate into electrons and holes  
under the appropriate circumstances, thus generating an electric current.

40 The eleventh embodiment of the invention relates to metal-insulator-  
semiconductor field effect transistors comprising one or more of the copolymers of the  
invention (serving as the semiconducting polymer) deposited onto an insulator wherein  
45 the copolymers are present as single-layer films or as multiple-layer films whose  
combined thickness is in the range of 10 nm to 1000 nm, preferably in the range of 25 nm  
to 500 nm, most preferably in the range of 50 nm to 300 nm. The copolymer films may  
50 be formed by solvent-based processing techniques such as spin-coating, roller-coating,  
dip-coating, spray-coating and doctor-blading. When two or more copolymers are used,

5 they may be deposited separately as distinct layers or deposited as one layer from a  
solution containing a blend of the desired copolymers. Two electrodes (source and drain)  
are attached to the semiconducting polymer and a third electrode (gate) onto the  
10 opposite surface of the insulator. If the semiconducting polymer is hole transporting (that  
is, the majority carriers are positive holes), then applying a negative DC voltage to the  
gate electrode induces an accumulation of holes near the polymer-insulator interface,  
15 creating a conduction channel through which electric current can flow between the source  
and the drain. The transistor is in the "on" state. Reversing the gate voltage causes a  
depletion of holes in the accumulation zone and cessation of current. The transistor is in  
20 the "off" state. If the semiconducting polymer is electron transporting (that is, the majority  
carriers are electrons), then applying a positive DC voltage to the gate electrode induces  
a deficiency of holes (accumulation of electrons) near the polymer-insulator interface,  
creating a conduction channel through which electric current can flow between the source  
and the drain.

25 15 The copolymers of instant invention may be prepared by a variety of  
polycondensation processes. Particularly effective are those processes involving  
coupling of aromatic/vinyl/acetylenic monomers catalyzed by transition metals such as  
nickel and palladium.

30 Coupling of aryl and vinyl halides with zerovalent nickel was reported by  
20 Semmelhack et. al., (J. Am. Chem. Soc., Vol. 103, 1981, p. 6460-6471). Coupling of  
aryl halides and other heteroaromatic halides with zerovalent nickel was discussed by  
35 Yamamoto et. al., (Macromolecules, Vol. 25, 1992, p. 1214-1223). These procedures  
require a large excess of the air and moisture sensitive zerovalent nickel. A variant that  
requires a truly catalytic amount of nickel but a large excess of zinc as the reducing agent  
25 was first reported by Colon et. al., (J. Polym. Sci., Polym. Chem., Vol. 28, 1990, p. 367-  
383), and later applied successfully to fully conjugated polymers by Ueda et. al.,  
(Macromolecules, Vol. 24, 1991, p. 2694-2697), represents an improvement with respect  
40 to experimental handling. In these procedures, mixtures of monomers each bearing two  
halogen substituents (preferably bromine and chlorine) can be polymerized into  
45 30 copolymers of essentially random nature if the monomers are of about the same  
reactivity. If reactivities are significantly different, then the more reactive monomers  
would be polymerized preferentially over the less reactive ones. The result would be a  
50 somewhat "blocky" copolymer of uncertain structure and order. An additional  
disadvantage of these procedures is the presence of large amounts of metallic reagents

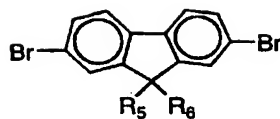
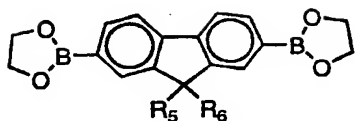
5 which must often be thoroughly removed from the resulting copolymers to avoid the deleterious effects they can have on electronic device performance.

10 Coupling reactions catalyzed by palladium are usually more preferred as the amount of palladium required is truly catalytic and the structure and order of the resulting  
5 copolymers are more predictable. Chen et. al., (Macromolecules, Vol. 26, 1993, p. 3462-3463), produced regiospecific polythiophenes by palladium catalyzed coupling of 2-bromo-5-(bromozinco)alkylthiophenes. The obtained molecular weights were very low,  
15 however. Coupling of aryl halides with acetylenes catalyzed by palladium was successfully used for producing copolymers by Yamamoto et. al., (Macromolecules, Vol. 27, 1994, p. 6620-6626), and coupling of aryl halides with olefins similarly employed for  
10 polymerization by Greiner et. al., (Macromol. Chem. Phys., Vol. 197, 1996, p. 113-134).

20 A preferred condensation reaction involves the coupling of organoboron compounds with organohalides as taught by Miyaura and Suzuki (Chemical Reviews, Vol. 95, 1995, p. 2457-2483). This reaction has been adapted with improvement to the  
25 production of high molecular weight polymers by Inbasekaran et. al., as reported in U.S. Patent 5,777,070. Polymerization is effected by reacting a near equimolar mixture of an aromatic/vinyl diboronic acid/ester (hereinafter referred to as type A monomer) and an aromatic/vinyl dibromide (hereinafter referred to as type B monomer). Two or more  
30 type A monomers and two or more type B monomers may be used so long as the combine molar amounts of A's are approximately equal to that of B's. A unique feature of copolymers from this process is the order which results from the fact that chain growth  
20 takes place exclusively via the formation of A-B dyads as each type A monomer can only react with a type B monomer. Monomers of more complex structures may be advantageously employed to yield copolymers of even higher degree of structural order.  
35 For example, an appropriately functionalized electron transporting RMU may be reacted with two molecules of a hole transporting moiety to yield a new monomer of the structure Br-HTRMU-ETRMU-HTRMU-Br, where HTRMU and ETRMU stand for hole transporting RMU and electron transporting RMU respectively.

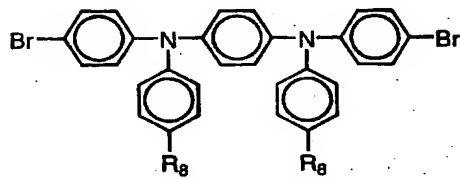
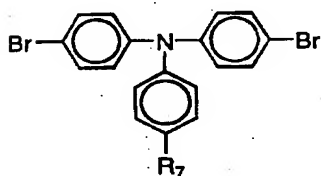
40 The following specific embodiments are given to illustrate the invention and  
45 should not be interpreted as limiting in any way.

50 All inherent viscosity measurements were determined on THF solutions (0.5 g/dL) at 25°C and are expressed in unit of dL/gram. The formulas of the monomers used are given below.



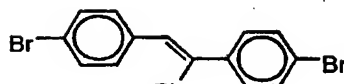
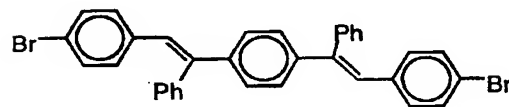
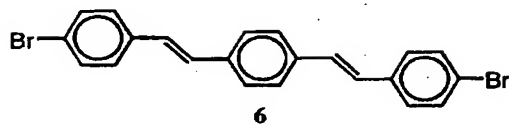
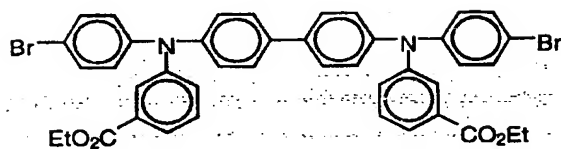
1a,  $R_5 = R_6 = n\text{-butyl}$   
 1b,  $R_5 = R_6 = n\text{-hexyl}$   
 1c,  $R_5 = R_6 = n\text{-octyl}$   
 1d,  $R_5 = R_6 = 2\text{-ethylhexyl}$   
 1e,  $R_5 = R_6 = n\text{-undecyl}$   
 1f,  $R_5 = R_6 = n\text{-dodecyl}$

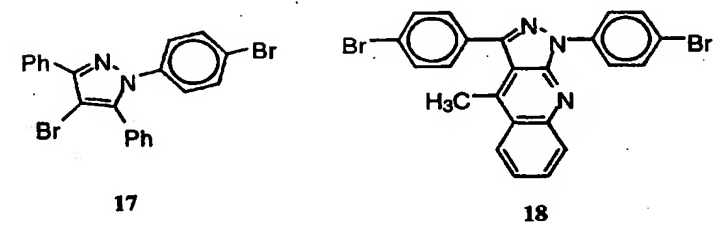
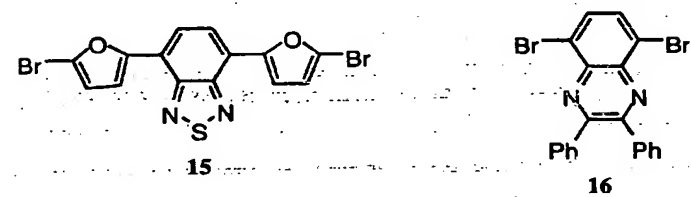
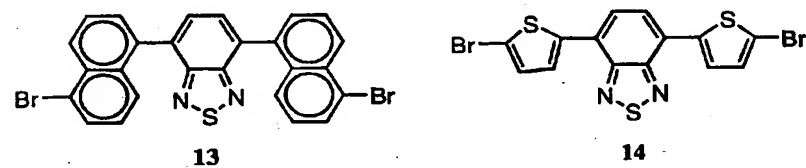
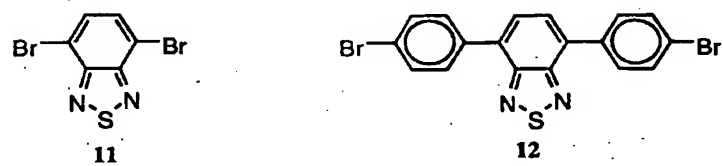
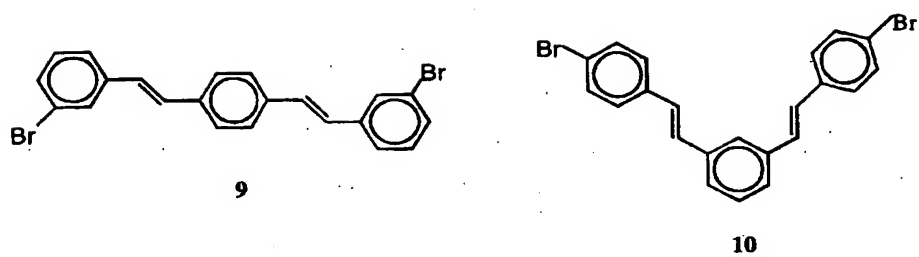
2b,  $R_5 = R_6 = n\text{-hexyl}$   
 2c,  $R_5 = R_6 = n\text{-octyl}$   
 2d,  $R_5 = R_6 = 2\text{-ethylhexyl}$

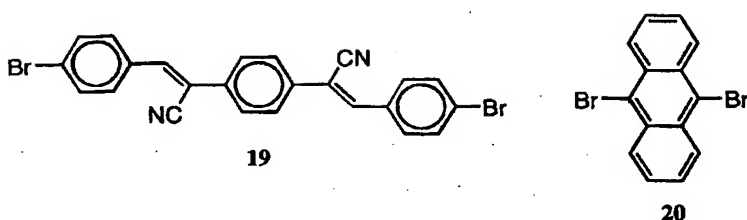


3a,  $R_7 = \text{sec-butyl}$   
 3b,  $R_7 = \text{methoxy}$

4a,  $R_7 = \text{methyl}$   
 4b,  $R_7 = \text{methoxy}$







Monomers 2-5 and 11 are known compounds (see WO 97/33193 and U.S. Patent 5,777,070), and monomer 20 is commercially available. Procedures for the preparation of other monomers used in the following examples are given below. All compounds exhibit spectral data consistent with their structures.

General Procedure for the Preparation of 9,9-Disubstituted 2,7-Fluorene Diboronates (1)

To a stirred mixture of 9,9-disubstituted 2,7-dibromofluorene (10 mmol) and 50 mL of tetrahydrofuran (THF) under nitrogen at  $-78^{\circ}\text{C}$  was added dropwise a 2.5 M solution of n-butyllithium in hexanes (8 mL, 20 mmol) over 10 min. The di-lithio intermediate precipitated in a few minutes and the resulting colorless suspension was stirred at  $-78^{\circ}\text{C}$  for 1 hr. Tri-isopropylborate (7.5 g, 40 mmol) was added all at once, and the resulting slurry (additional 20-30 mL of THF added to facilitate agitation, in some cases) was stirred for 1 hr at  $-78^{\circ}$ , 16 hours at room temperature, and poured into 300 mL of ice-water containing 25 mL of conc. HCl. After stirring for 30 min, the product was extracted with 2x150 mL of diethyl ether. The ether extracts were washed with saturated aqueous sodium chloride solution (200 mL), dried ( $\text{MgSO}_4$ ) and rotary evaporated to remove the solvent providing the diboronic acid as a semi-solid. The purity of the crude diboronic acid was assessed to be 85-95 percent depending upon the substrate by HPLC analysis and was converted to the diboronate without further purification, as described below.

The crude diboronic acid was suspended in 50 mL of toluene and 30 mmol (1.86 g) of ethylene glycol, and the mixture was stirred and refluxed under a Dean-Stark trap for 2-3 hr. During this time, about 25 mL of toluene was collected as over-head along with a small amount of water formed during the reaction as an azeotrope. The reaction mixture was cooled and the solvent was removed. The residue (semi-solid) was recrystallized from hexane or toluene-hexane mixture, depending upon the substrate, to provide the diboronate as colorless, amorphous powder in 70-85 percent overall yield.

5 The purity, as judged by HPLC, was about 95-99 percent. Further recrystallization provided material of 99+ percent purity.

10 4,4'-Dibromo-1,4-distyrylbenzene (6)

15 To a stirred mixture of p-xylylenebis-(triphenylphosphonium bromide) (8.05 g, 10 mmol) and 4-bromobenzaldehyde (3.75 g, 20 mmol) in ethanol (100 mL) under nitrogen was added dropwise a solution of lithium ethoxide (1.0 M in ethanol, 21.5 mL, 21.5 mmol). The reaction was stirred at ambient temperature for 6 hours. The precipitate was filtered, washed with ethanol and dried. The crude product was redissolved in toluene, washed successively with aqueous hydrochloric acid (5 percent) and water and dried with magnesium sulfate. The solvent was evaporated under vacuum and the residue was recrystallized from toluene/methanol to afford 3.6 g (82 percent) of white solid. NMR indicated a trans-trans structure and the purity was found to be 100 percent as shown by HPLC.

25 4,4'-Dibromo-b,b'-diphenyl-1,4-distyrylbenzene (7)

30 To a stirred mixture of tetraethyl-o-xylylenediphosphonate (9.4 g, 25.0 mmol) and 4-bromobenzophenone (13.1 g, 50.0 mmol) in toluene was added potassium tert-butoxide (6.2 g, 55.0 mmol). The reaction was stirred at ambient temperature for 6 hours. The solution was filtered through a layer of celite. The solvent was evaporated under vacuum and the residue was recrystallized from toluene/hexane to give 5.8 g (39 percent) of light yellow solid material which was found to be a 1:4 mixture of the cis-trans and trans-trans isomers by HPLC.

35 1,2-Bis(4-bromophenyl)-1-phenylethylene (8)

40 To a stirred solution of 4-bromobenzophenone (5.22 g, 20 mmol) and diethyl-4-bromophenylphosphonate (6.8 g, 22 mmol) in 1,2-dimethoxyethane (60 mL) under nitrogen was added sodium hydride (0.52 g, 22 mmol) and the mixture was stirred and refluxed for 3 hours. After cooling, the mixture was poured into 150 g of ice water, the product was extracted with ether and purified by chromatography on silica gel. Elution with hexanes gave 6 grams (64 percent yield) of the title compound as a colorless oil which was found to be a 1:1 mixture of the cis and trans isomers.

50 3,3'-Dibromo-1,4-distyrylbenzene (9)

55 To a stirred mixture of p-xylylenebis-(triphenylphosphonium bromide) (15.8 g, 20 mmol) and 3-bromobenzaldehyde (7.4 g, 40.0 mmol) in ethanol (150 mL) under nitrogen

5 was added dropwise a solution of lithium ethoxide (1.0 M in ethanol, 41.0 mL, 41.0 mmol). The reaction was stirred at ambient temperature for 8 hours. The precipitate was filtered, washed with ethanol and dried. The crude product was redissolved in toluene,  
10 washed successively with aqueous hydrochloric acid (5 percent) and water and dried with magnesium sulfate. The solvent was evaporated under vacuum and the residue was recrystallized from toluene/ethanol to afford 4.9 g (56 percent) of off-white solid. The  
15 purity was found to be >99 percent as shown by HPLC.

4,4'-Dibromo-1,3-distyrylbenzene (10)

To a stirred mixture of m-xylylenebis-(triphenylphosphonium bromide) (15.8 g, 20  
10 mmol) and 4-bromobenzaldehyde (7.4 g, 40.0 mmol) in ethanol (200 mL) under nitrogen was added dropwise a solution of lithium ethoxide (1.0 M in ethanol, 41.0 mL, 41.0 mmol). The reaction was stirred at ambient temperature for 8 hours. The precipitate was filtered, washed with ethanol and dried. The crude product was redissolved in toluene,  
20 washed successively with aqueous hydrochloric acid (5 percent) and water and dried with magnesium sulfate. The solvent was evaporated under vacuum and the residue was recrystallized from toluene/ethanol to afford 3.8 g (43 percent) of yellow flakes which was  
25 found to be >99 percent in purity as shown by HPLC.

2,5-Di(4-bromophenyl)-2,1,3-benzothiadiazole (12)

A mixture of phenylboronic acid (17.6 g, 144.0 mmole), 4,7-dibromo-2,1,3-  
20 benzothiadiazole (21.0 g, 71.4 mmole), tetrakis(triphenylphosphine) palladium (180 mg, 0.156 mmol), Aliquat 336 (1.5 g), aqueous sodium carbonate (2 M, 100 mL) toluene (350 mL) was stirred and refluxed for 14 h under nitrogen. After cooling, the aqueous layer was separated, the organic layer was washed with water and dried. The solvent was removed and the residue was crystallized from toluene-ethanol give 11.4 g (55 percent)  
35 of the crystalline material.

To a stirred solution of above 2,5-diphenyl-2,1,3-benzothiadiazole (7.0 g, 30.6 mmol) in acetic acid (50 mL) was added dropwise bromine (13.7 g, 77.5 mmol). The reaction was stirred and refluxed for 8 hours. After cooling water (100 mL) was added  
45 and the reaction was allowed to stand at ambient temperature for 2 hours. The product was filtered, washed with water and dried. Recrystallized from toluene/ethanol afforded 9.3 g (68 percent) of yellow powder. The purity was found to be >98 percent as shown by  
50 NMR and HPLC.

2,5-Di(4-bromonaphthyl)-2,1,3-benzothiadiazole (13)

To a stirred solution of 2,5-dinaphthalenyl-2,1,3-benzothiadiazole [Prepared from naphthylboronic acid and 4,7-dibromo-2,1,3-benzothiadiazole by the procedure described in (12) for the preparation of 2,5-diphenyl-2,1,3-benzothiadiazole] (9.9 g, 25.5 mmol) in 1,4-dioxane (80 mL) was added dropwise bromine (12.4 g, 77.5 mmol). The reaction was stirred and refluxed for 6 hours. After cooling ethanol (100 mL) was added and the reaction was allowed to stand at ambient temperature for 10 hours. The product was filtered and washed with ethanol. Recrystallized from toluene/ethanol gave 9.2 g (66 percent) of yellow flakes. The purity was found to be >95 percent as shown by NMR and HPLC.

4,7-Bis (5-bromo-2-thienyl)-2,1,3-benzothiadiazole (14)

4,7-Dithien-2-yl-2,1,3-benzothiadiazole [prepared by reacting 4,7-dibromo-2,1,3-benzothiadiazole with tributyl(thien-2-yl)stannane by following published procedure (Kitamura et al., Chem. Mater., Vol. 8, 1996, p. 570-578)] (7.7 g, 25.7 mmol) was dissolved in a mixture of chloroform (200 mL) and acetic acid (200 mL) under nitrogen and N-bromosuccinimide (9.61 g, 54 mmol) was added all at once. After stirring the reaction mixture at RT all night, the dark red precipitate was filtered off and recrystallized from DMF twice to provide the title compound as shiny, red crystals (6.85 g, 58.2 percent) which had a purity of 100 percent as shown by HPLC analysis.

2,5-Di(5'-bromofuranyl)-2,1,3-benzothiadiazole (15)

To a stirred solution of 2,5-difuranyl-2,1,3-benzothiadiazole [prepared by reacting 4,7-dibromo-2,1,3-benzothiadiazole with 2-(tributylstannyl)furan by following published procedure (Kitamura et al., Chem. Mater., Vol. 8, 1996, p. 570-578)] (2.9 g, 10.1 mmol) in 1,4-dioxane (40 mL) was added dropwise bromine (3.6 g, 22.3 mmol). The reaction was stirred at ambient temperature for 5 minutes. The reaction was then diluted with water and the precipitate was filtered, washed with water and dried. The crude product was redissolved in toluene and chromatographed on a short alumina column. The solvent was evaporated under vacuum and the residue was recrystallized from toluene/ethanol to afford 3.0 g (70 percent) of red flakes which was found to be >99 percent in purity as shown by HPLC.

5,8-Dibromo-2,3-diphenylquinoxaline (16)

3,6-Dibromo-1,2-phenylenediamine (prepared by reduction of 4,7-dibromo-2,1,3-benzothiadiazole with zinc and acetic acid as reported by Naef and Balli (Helv. Chim. Acta, 1978, 61, 2959) (2 g, 8 mmol) and benzil (1.9 g, 9 mmol) were dissolved in 2-propanol (40 mL) and 5 drops of trifluoroacetic acid was added. The mixture was stirred and heated under reflux for 2 hr. On cooling, the pale yellow solid was filtered and recrystallized from ethanol to give 2.7 g (75 percent) of the title compound as colorless solid, mp 221-223°C.

4-Bromo-1-(4-bromophenyl)-3,5-diphenylpyrazole (17)

The title compound was obtained by the bromination of 1-(4-bromophenyl)-3,5-diphenylpyrazole (obtained by reacting dibenzoylmethane and 4-bromophenyl hydrazine in acetic acid) with N-bromosuccinimide in DMF at 65°C for 1 hr. The crude product was recrystallized from ethanol to provide the title compound as colorless powder in 72 percent yield and the purity was 100 percent as shown by HPLC.

1,3-Bis(4-bromophenyl)-4-methyl-1H-pyrazolo[3,4-b]quinoline (18)

A mixture of 1,3-bis(4-bromophenyl)-pyrazolin-5-one (7.9 g, 20 mmol) and o-aminoacetophenone (2.7 g, 20 mmol) in 30 mL of ethylene glycol was heated and stirred at 180°C under nitrogen for 22 hr. The dark red solution was cooled, 40 mL of ethanol added, refluxed for 1 hr and cooled. The yellow solid was filtered and recrystallized from toluene-hexane to provide 2.3 g (26 percent yield) of the title compound as yellow crystals. The purity was found to be 100 percent as shown by HPLC.

a,a-Bis(4-bromophenylmethylene)-1,4-benzenediacetonitrile (19)

A mixture of 4-bromobenzaldehyde (24.0 g, 0.13 mole), phenylene-1,4-diacetonitrile (10.0 g, 0.064 mole), piperidine (5 mL), and ethanol (150 mL) was refluxed for 3 h and the mixture allowed to stand overnight at room temperature. The orange crystalline solid was filtered and washed three times with ethanol (200 mL) and dried to give 15.3 g (50 percent) of the desired product. The <sup>1</sup>H nmr spectrum is consistent with the structure of the desired product. Recrystallization from DMF provided a very pure product for polymerization.

The copolymers of the invention were prepared by the procedure of U.S. Patent 5,777,070 except those involving monomer 14 which required THF as a cosolvent. The

structures and monomeric reactants of the exemplified copolymers are given in Table 1;  
the properties of copolymers are given in Table 2.

Table 1. Compositions of Fluorene Copolymers.

Copolymer	Copolymer Empirical Formula <sup>A</sup>	Monomer (mmoles)	Monomer (mmoles)	Monomer (mmoles)	Monomer (mmoles)
1	$-[(1c)_{36}-(3a)_2-(4b)_3]_n-$	1c (10.2)	2c (7.5)	3a (1.0)	4b (1.5)
2	$-[(1c)_{20}-(11)_{17}-(20)_3]_n-$	1c (10.2)	11 (8.5)	20 (1.5)	
3	$-[(1c)_2-(11)_1-(3a)_1]_n-$	1c (8.2)	11 (4.0)	3a (4.0)	
4	$-[(1b)_1-(11)_2-(3a)_1]_n-$	1b (12.3)	11 (8.0)	3a (4.0)	
5	$-[(1b)_4-(11)_1-(3a)_1]_n-$	1b (12.3)	11 (9.0)	3a (3.0)	
6	$-[(1b)_3-(11)_1-(3b)_2]_n-$	1b (12.3)	11 (4.0)	3b (8.0)	
7	$-[(1b)_2-(12)_1-(3a)_1]_n-$	1b (10.2)	12 (5.0)	3a (5.0)	
8	$-[(1b)_2-(13)_1-(3a)_1]_n-$	1b (8.2)	13 (4.0)	3a (4.0)	
9	$-[(1b)_{34}-(5)_1-(11)_1]_n-$	1b (10.2)	2b (7.0)	5 (2.5)	11 (0.5)
10	$-[(1c)_2-(16)_1-(3a)_1]_n-$	1c (3.5)	16 (1.7)	3a (1.7)	
11	$-[(1c)_{10}-(2c)_1-(20)_1-(4b)_2]_n-$	1c (10.2)	2c (5.0)	20 (3.0)	4b (2.0)
12	$-[(1b)_{10}-(3a)_2-(20)_3]_n-$	1b (10.2)	2b (5.0)	3a (2.0)	20 (3.0)
13	$-[(1f)_3-(1c)_2-(19)_1]_n-$	1f (3.0)	2c (2.0)	19 (1.0)	
14	$-[(1c)_{18}-(19)_1]_n-$	1c (4.0)	2c (3.6)	19 (0.4)	
15	$-[(1c)_{39}-(19)_1]_n-$	1c (4.0)	2c (3.8)	19 (0.2)	
16	$-[(1f)_2-(1d)_1-(1e)_1-(19)_3]_n-$	1f (2.1)	1d (1.0)	2c (1.0)	19 (2.0)
17	$-[(1c)_1-(18)_1]_n-$	1c (4.1)	18 (4.0)		
18	$-[(1c)_{19}-(17)_1]_n-$	1c (8.2)	17 (8.0)		

Table 1. Continued. Compositions of Fluorene Copolymers.

Copolymer	Copolymer Empirical Formula <sup>a</sup>	Monomer (mmoles)	Monomer (mmoles)	Monomer (mmoles)	Monomer (mmoles)
19	-[(1c) <sub>10</sub> -(11) <sub>8</sub> -(14) <sub>1</sub> ]-	1c (8.2)	11 (7.2)	14 (0.8)	
20	-[(1c) <sub>4</sub> -(11) <sub>3</sub> -(14) <sub>1</sub> ]-	1c (5.2)	11 (3.8)	14 (1.2)	
21	-[(1e) <sub>2</sub> -(11) <sub>1</sub> -(14) <sub>1</sub> ]-	1e (2.6)	11 (1.3)	14 (1.3)	
22	-[(1c) <sub>100</sub> -(11) <sub>97</sub> -(14) <sub>1</sub> ]-	1c (8.2)	11 (7.8)	14 (0.2)	
23	-[(1c) <sub>20</sub> -(11) <sub>17</sub> -(14) <sub>1</sub> ]-	1c (6.2)	11 (5.1)	14 (0.9)	
24	-[(1c) <sub>7</sub> -(11) <sub>2</sub> -(14) <sub>1</sub> ]-	1c (5.1)	2b (2.0)	11 (2.0)	14 (1.0)
25	-[(1c) <sub>10</sub> -(11) <sub>1</sub> -(15) <sub>1</sub> ]-	1c (10.3)	15 (1.0)	11 (9.0)	
26	-[(1c) <sub>1</sub> -(8) <sub>1</sub> ]-	1c (11.0)	8 (10.8)		
27	-[(1c) <sub>1</sub> -(6) <sub>1</sub> ]-	1c (10.3)	6 (10.0)		
28	-[(1d) <sub>1</sub> -(6) <sub>1</sub> ]-	1d (10.3)	6 (10.0)		
29	-[(1c) <sub>1</sub> -(10) <sub>1</sub> ]-	1c (10.3)	10 (10.0)		
30	-[(1c) <sub>1</sub> -(9) <sub>1</sub> ]-	1c (10.3)	9 (10.0)		
31	-[(1c) <sub>1</sub> -(7) <sub>1</sub> ]-	1c (9.9)	7 (9.6)		
32	-[(1c) <sub>10</sub> -(2b) <sub>7</sub> -(20) <sub>1</sub> ]-	1c (10.2)	2b (7.0)	20 (3.0)	

<sup>a</sup> Bold type numerals in copolymer empirical formulas refer to RMUs of the corresponding monomers.

Table 2. Properties of Fluorene Copolymers.

Copolymer	T <sub>g</sub> (°C)	Inherent Viscosity	Absorption <sup>a</sup> (nm)	Fluorescence <sup>b</sup> (nm)	Bandgap (eV)
1	-	1.50	383	467	
2	108	1.33	323 462	535	
3	100	1.27 <sup>c</sup>	346, 384 459	535	
4	108	0.95 <sup>d</sup>	339, 393 466	545	
5	125	1.18	320, 339 461	550	
6	140	0.52	336, 383 450	558	
7	195	3.00	352 348	544	
8	201	1.10	383	524	
9	136	1.70	381	531	
10	125	0.52	342 389	507	
11	81	1.00	388	480	
12	-	0.45	383	431	2.89
13	131	0.57	390	500	
14	108	0.78	390	510	2.62
15	97	0.85	390	510	2.71
16	102	0.94	420	515	2.52
17	-	0.95	355	497	
18	-	0.21	347	420 525	
19	120	1.82	322, 467 560	642	2.10
20	132	1.25	341, 474 550	639	
21	105	1.41	389, 460 570	659	
22	103	1.43	322 465	666	
23	125	1.24	320, 470 556	646	

Table 2. Continued. Properties of Fluorene Copolymers.

Copolymer	T <sub>g</sub> (°C)	Inherent Viscosity	Absorption <sup>a</sup> (nm)	Fluorescence <sup>b</sup> (nm)	Bandgap (eV)
24	112	1.15	383, 463 550	639	
25	119	1.1	325 339	630	
26	82	0.31	375	441 470	
27	135	0.55	373	456 483	2.76
28	134	0.33	388	440 475	2.75
29	101	0.23	359	433	2.95
30	92	0.25	335	428	3.20
31	134	0.30	381	492	2.68
32	130	1.73	384	440	

<sup>a</sup> Absorption peaks of copolymer films<sup>b</sup> Fluorescence peaks of copolymer films<sup>c</sup> Weight-average molecular weight 97,000 by light scattering<sup>d</sup> Weight-average molecular weight 53,000 by lightLight Emitting Diodes (LED)

ITO-coated glass with sheet resistance of about 15 ohms/square was used as substrate for diode fabrication. The ITO side of the substrate was treated with a 100 nm coating of Baytron P™ (a conducting polymer available from Bayer A.G.) diluted with either equal part or two parts of poly(styrenesulfonic acid). The conducting polymer film was dried at 200°C in air for about 5 minutes and was then coated with an light emitting polymer film by spin-coating with solutions of polymers in xylene. The light emitting polymer film was then dried in a nitrogen atmosphere at 90°C for at least two hours. Onto the light emitting polymer film was then deposited a calcium cathode (about 75 - 100 nm). The finished device was connected to a power source, in an inert atmosphere,

with ITO being the positive electrode. Luminance of emitted light and density of current flowing through the diode were monitored as a function of applied voltage. Luminance is expressed in unit of  $\text{Cd/m}^2$ , and efficiency expressed as lumens/watt (L/W):  $L/W = p$  ( $\text{Cd/A}$ )/V where A and V are respectively the current and voltage for a given brightness.

#### 5 Green LEDs.

Table 3 lists the compositions and voltages and efficiency at  $4000 \text{ Cd/m}^2$  of 3 green LEDs, two of which contain copolymers of the invention. Green 1 and Green 2, of approximately the same performance, reaching luminance of  $4000 \text{ Cd/m}^2$  at lower voltage and higher efficiency than the comparative LED which does not contain copolymer of the invention. The copolymer of the comparative example differs from copolymers 4 and 5 in the absence of a hole transporting RMU, thus illustrating the advantage of achieving a balance in hole and electron transport properties. Note the same benefit is realized in the blend (Green 2) containing a copolymer of the invention.

Table 3. Green LEDs

Example	Copolymer Film : Structure <sup>A</sup>	4000 $\text{Cd/m}^2$	
		Volts	L/W
Green 1	100 nm copolymer 5: $-\{(\text{1b})_4-(\text{11})_3-\text{3a}\}-$	3.9	2.36
Comparative	100 nm comparative copolymer: $-\{1\text{b}-11\}-$	6.3	0.56
Green 2	75 nm blend of 30 weight percent comparative copolymer in copolymer 4. Comparative copolymer: $-\{1\text{b}-11\}-$ Copolymer 4: $-\{(\text{1b})_4-(\text{11})_3-\text{3a}\}-$	3.7	2.95

<sup>A</sup> Bold type numerals in copolymer empirical formulas refer to RMUs of the corresponding monomers.

#### 40 Red LEDs.

Table 4 lists two LEDs that emit red light. Red 1 is based on a single copolymer while Red 2 is based on a blend of two copolymers of the invention. The marked improvement in device performance noted in Red 2 over Red 1 demonstrates the advantages of using polymer blends.

Table 4. Red LEDs

Example	Copolymer Film : Structure <sup>A</sup>	1000 Cd/m <sup>2</sup>	
		Volts	L/W
Red 1	75 nm copolymer 19: -[(1c) <sub>100</sub> -(11) <sub>0</sub> ]-14-	9.0	0.12
Red 2	75 nm blend of 30 weight percent copolymer 19 in copolymer 5.	5.0	0.41

<sup>A</sup> Bold type numerals in copolymer empirical formulas refer to RMUs of the corresponding monomers.

White LED

Two white LEDs each based on a 100 nm film of a blend containing copolymer 22 of the invention in a mixture of fluorene copolymers not of this invention (hereinafter referred to as comparative mixture). The comparative mixture is a blend of

15 weight percent of fluorene copolymer -[1c-4a]-

7 weight percent of fluorene copolymer -[1c-3a]-

78 weight percent of fluorene homopolymer -[1c]-

The amount of copolymer 22 and LED performance are provided in Table 5. The comparative mixture without copolymer 22 is a blue light emitter and the addition of 1 weight percent or less of copolymer 22 of the invention converts the blend into a white light emitter. This example illustrates the impact an extremely small amount of a copolymer of the invention can have on LEDs.

Table 5. White LEDs

Example	Copolymer of invention in blend <sup>A</sup>	1500 Cd/m <sup>2</sup>	
		Volts	L/W
White 1	0.5 weight percent copolymer 22, -[(1c) <sub>100</sub> -(14) <sub>3</sub> ]-, in blend	10.8	0.2
White 2	1.0 weight percent copolymer 22, -[(1c) <sub>100</sub> -(14) <sub>3</sub> ]-, in blend	8.9	0.3

<sup>A</sup> Bold type numerals in copolymer empirical formulas refer to RMUs of the corresponding monomers.

## Claims

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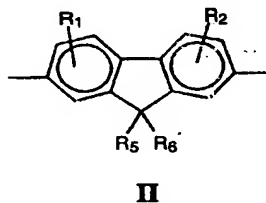
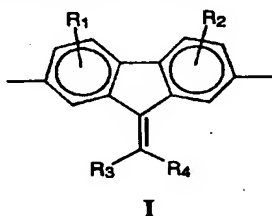
**CLAIMS:**

1. A copolymer comprising monomeric units and further characterized by having

(a) at least 10 percent of the monomeric units are fluorene moieties selected from 9-substituted fluorene moieties, 9,9-disubstituted fluorene moieties or combinations thereof; and

(b) at least 1 percent of the monomeric units comprising two other moieties which are different from each other but which both comprise delocalized  $\pi$ -electrons; the other moieties being independently selected from the group consisting of moieties that have hole transporting properties and moieties that have electron transporting properties; wherein if both of the two other moieties have hole transporting properties, then at least one of said moieties is derived from stilbenes or 1,4-dienes without electron withdrawing substituents, N,N,N',N'-tetraarylbenzidines, N-substituted-carbazoles, diarylsilanes, and thiophenes/furans/pyrroles without electron-withdrawing substituents.

2. The copolymer of Claim 1 wherein the fluorene moieties are selected from groups having the formulas:



wherein,  $R_1$  and  $R_2$  are independently in each occurrence hydrogen,  $C_{1-20}$  hydrocarbyl,  $C_{1-20}$  hydrocarbyloxy,  $C_{1-20}$  thiohydrocarbyloxy, or cyano

$R_3$  and  $R_4$  are independently in each occurrence a hydrogen,  $C_{1-20}$  hydrocarbyl optionally substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters;  $C_{6-20}$  aryl optionally substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters; or  $R_3$  and  $R_4$  form  $C_{9-12}$  cyclic structures with the olefin carbon to which they are attached, said cyclic structures optionally further contain one or more heteroatoms such as phosphorus, sulfur, oxygen and nitrogen;

5  $R_1$  and  $R_2$  are independently in each occurrence a hydrogen,  $C_{1-20}$  hydrocarbyl  
optionally substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary  
amines, hydroxy, carboxylic/sulfonic acids, cyano, and esters;  $C_{6-20}$  aryl optionally  
10 substituted with  $C_{1-20}$  alkoxy/aryloxy, thioalkoxy/thioaryloxy, secondary/tertiary amines,  
5 hydroxy, carboxylic/sulfonic acids, cyano, and esters; or  $R_3$  and  $R_4$  form  $C_{3-12}$  cyclic  
structures with the C-9 carbon of fluorene, said cyclic structures optionally further contain  
one or more heteroatoms such as phosphorus, sulfur, oxygen and nitrogen.

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20 3. The copolymer of Claim 1 wherein at least 15 percent of the monomeric units  
10 are the fluorene moieties and at least 10 percent of the monomeric units are two moieties  
which have hole transporting properties.

25 4. The copolymer of Claim 1 wherein at least 15 percent of the monomeric units  
15 are the fluorene moieties and at least 10 percent of the monomeric units are two moieties  
which have electron transporting properties.

30 5. The copolymer of Claim 1 wherein the moieties having electron transporting  
properties are selected from moieties comprising electron-withdrawing groups.

35 20 6. The copolymer of Claim 1 wherein at least 1 percent of the monomeric units  
comprise hole transporting moieties and at least 1 percent of the monomeric units  
comprise electron transporting moieties.

40 25 7. The copolymer of Claim 6 wherein at least 15 percent of the monomeric units  
are the fluorene moieties, at least 5 percent of the monomeric units have hole  
transporting properties, and at least 5 percent of the monomeric units have electron  
transporting properties.

45 30 8. A copolymer comprising monomeric units and further characterized in that

50 (a) at least 10 percent of the monomeric units are fluorene moieties selected  
from 9-substituted fluorene moieties, 9,9-disubstituted fluorene moieties or combinations  
thereof; and

5 (b) at least 1 percent of the monomeric units are independently selected in each occurrence from the group consisting of moieties that have hole transporting properties and moieties that have electron transporting properties; and

10 (c) at least 1 percent of the monomeric units are derived from substituted or unsubstituted benzene, naphthalene, and biphenylene, wherein if a substituted compound is used the substituents are selected from alkyl or alkoxy groups having 1 to 12 carbon atoms and aryl or aryloxy groups having 6 to 10 carbon atoms.

15 9. A composition comprising a blend of a first polymer, which is selected from the copolymer of Claim 1 and the copolymer of Claim 8, with a second polymer.

20 10. The composition of Claim 9 wherein the second polymer comprises monomeric units selected from 9-substituted fluorene moieties, 9,9-disubstituted fluorene moieties, and combinations thereof.

25 11. The composition of Claim 9 wherein the second polymer is a copolymer as defined in Claim 1 and is different from the first polymer.

30 12. The composition of Claim 9 wherein the first polymer is present in an amount of at least 0.1 weight percent based on total weight of the composition.

35 13. A film comprising at least 0.1 percent by weight of a polymer selected from the copolymer of Claim 1 and the copolymer of Claim 8.

40 14. A light emitting diode comprising an anode, a cathode, and at least one film of Claim 13 located between the anode and the cathode.

45 15. The light emitting diode of Claim 14 wherein the anode comprises a mixed oxide of tin and indium and the cathode comprises a metallic film.

50 16. A photocell comprising at least one film of Claim 13.

55 17. The photocell of Claim 16, wherein the at least one film is located between a transparent or semi-transparent first electrode and a second electrode.

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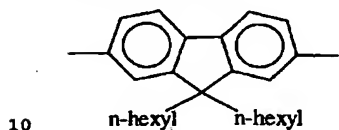
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18. A metal-insulator-semiconductor field effect transistor comprising an insulating layer, at least one film of Claim 13 deposited onto that substrate, a source electrode connected to a first portion of the at least one film, a drain electrode connected to a second portion of the at least one film, and a gate electrode located on the opposite side of the insulating layer from the at least one film.

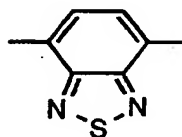
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19. A composition comprising a copolymer which comprises the following monomeric units:

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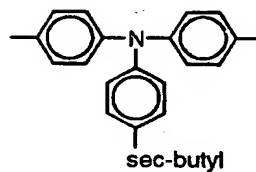
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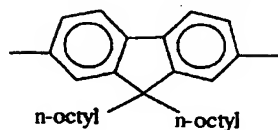
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20. A light emitting diode comprising a film comprising the composition of Claim 19.

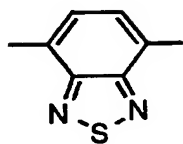
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21. A composition comprising a copolymer having the following monomeric units:

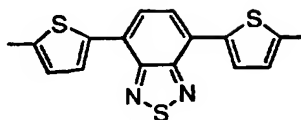
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and



20 22. A light emitting diode comprising a film comprising the composition of Claim

5 21.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PL./US 99/07876

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09K11/06 C08G61/10 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K H01L C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 777 070 A (INBASEKARAN MICHAEL ET AL) 7 July 1998 (1998-07-07) cited in the application column 3, line 50,51 examples 2,5	1-21
A	WO 97 05184 A (DOW CHEMICAL CO) 13 February 1997 (1997-02-13) example 28	1-21
A	FR 2 702 870 A (THOMSON CSF) 23 September 1994 (1994-09-23) figures 10A,10B	1,2
A	WO 97 33193 A (DOW CHEMICAL CO) 12 September 1997 (1997-09-12) page 10, line 19 - line 23	1,2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 September 1999

Date of mailing of the international search report

06/10/1999

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Paalman, R

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/07876

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5777070 A	07-07-1998	WO 9920675 A	29-04-1999
WO 9705184 A	13-02-1997	US 5708130 A	13-01-1998
		CN 1192223 A	02-09-1998
		EP 0842208 A	20-05-1998
FR 2702870 A	23-09-1994	NONE	
WO 9733193 A	12-09-1997	AU 2277697 A	22-09-1997
		US 5929194 A	27-07-1999

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